

## Speleothems

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## Chapter 7 SPELEOTHEMS

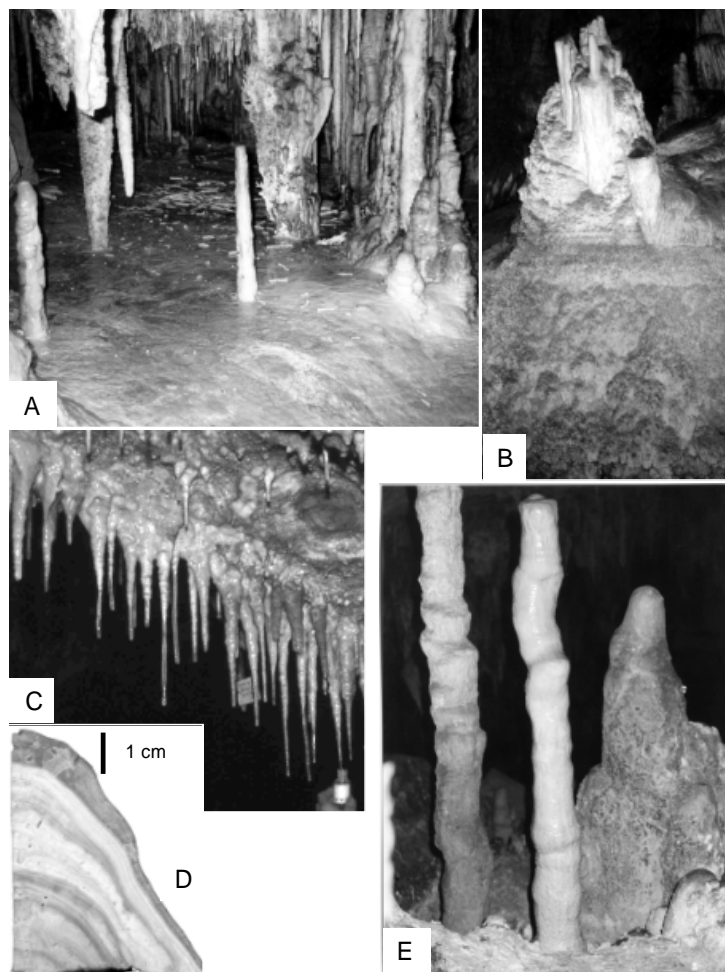
### 7.1 Introduction to speleothem-forming cave environments

#### 7.1.1 The scope and purpose of this chapter

Speleothems are mineral deposits formed in caves, typically in karstified host rocks (Gunn, 2004). The cave environment is arguably an extension of the surface landscape, because caves are defined as cavities large enough for humans to enter (Hill and Forti, 1997). Speleothem deposits are controlled not only by the distribution, quantity and chemistry of water percolating through the karstic aquifer (a property strongly influenced by the surface geomorphology and macroclimate), but also by the cave's peculiar microclimate, which in turn is controlled by cave geometry, aquifer properties and external microclimates. Despite the abundance of process research, there has been a relative lack of emphasis on the dynamic behaviour of aquifer and cave environments, which has hindered the production of integrated models.

Research on karst terrains has focused mainly on surface geomorphology, the geometry of cave systems, the hydrology and hydrogeochemistry of major springs, and the dating of cave development and the major phases of speleothem formation (Jennings, 1971, 1985; Sweeting, 1972, 1981; White, 1988; Ford and Williams, 1989). Since 1990, rapid progress in the development of proxies for palaeoclimate from calcareous speleothems has occurred (Gascoyne, 1992, cf. White, 2004 and McDermott, 2004). Pioneering work in this area, from Hendy and Wilson (1968) onwards, was published in leading journals and the same is true of much recent work (Yuan *et al.* [2004]; Wang *et al.* [2004] amongst many others). An unfortunate side-effect of this success is that, through pressure of space or interest, authors typically focus on their time series results without describing the geomorphic context of the material. Even in the longer accounts in international journals, this context is often not systematically described. Conversely, much high-quality work on karst geomorphology and hydrology has been published in national speleological journals or conference publications, poorly accessible to general readers. Hence, there is a danger that the spectacular contribution that speleothem studies are currently making to palaeoclimate research may be undermined by a lack of understanding of the complexities of cave environments by other climate researchers. Even speleothem workers themselves could be tempted to forget the original context of the speleothem on the laboratory bench. This accounts for the focus of this chapter, which is on calcareous speleothem formation in their geomorphic (including hydrogeological) context, with particular emphasis on issues related to palaeoclimate determination. Hence we focus on particular speleothem forms (Fig. 7.1): stalactites (ceiling-growths from cave drips), stalagmites (floor-growths from cave drips) and flowstones (speleothem sheets from thin water flows on walls or floors). For examples of the palaeoclimate time series themselves see Richards and Dorale (2003), Harmon

*et al.* (2004), White (2004), McDermott (2004), Fairchild *et al.* (2006) and references therein.



**Figure 7.1:** *Speleothem characteristics.* (A) Nerja cave, SE Spain. Highly-decorated cave chamber (view around 1.5 m across) with various stalactites and stalagmites (some joined into columns) with an intervening flowstone sheet. Debris of fallen, fast-growing soda straw stalactites on flowstone in background. (B) Nerja Cave. Phreatic pool deposits, with former water levels shown by horizontal lines, capped by more recent stalagmites. (C) Crag cave, SW Ireland. Line of stalactites (some are soda straws in their lower parts) representing water seepage from a fracture. Scale shown by collecting bottle, lower right and by the 5 mm minimum diameter of stalactites. (D) Ernesto cave, NE Italy. Section through conical stalagmite ER78, Ernesto cave (Frisia *et al.*, 2003); the darker top portion post-dates the year 1860. (E) Nerja Cave. Group of stalagmites; height of view approximately 50 cm. The two cylindrical or “candle-shaped” stalagmites to left show evidence of slight shifts in the lateral position of dripping water over time; the right-hand stalagmite has a more conical morphology, which could reflect either a higher drip rate or a larger fall height. The central stalagmite has a moist surface and may be currently active.

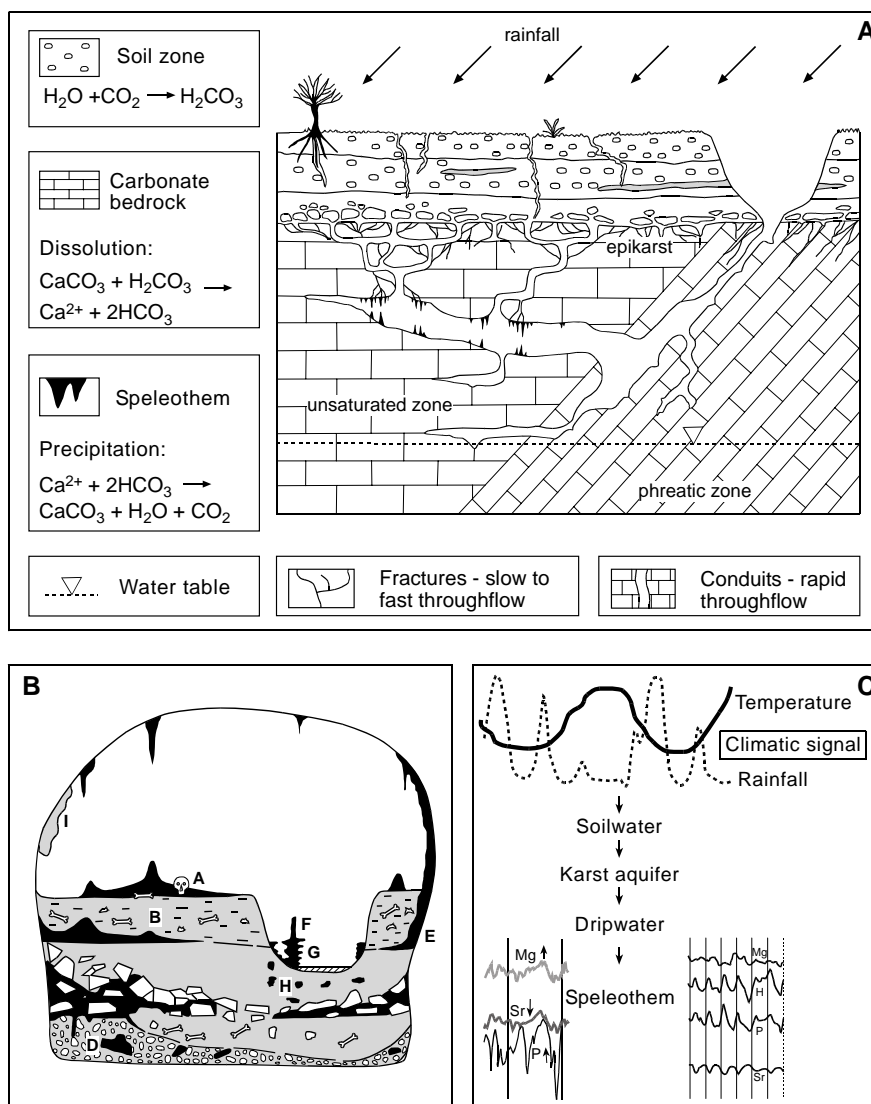
### 7.1.2 The CO<sub>2</sub>-degassing paradigm for calcareous speleothem formation

Just as one can refer to a planetary physiology (Lovelock, 1988), so the key processes of CO<sub>2</sub> creation, transport and exhalation responsible for calcareous speleothem formation (Fig. 7.2A) exemplify cave physiology. Shaw (1997) gave a meticulous review of the development of understanding of this issue from the eighteenth to the early twentieth century, including the realisation that solutes were derived principally by reaction with soil CO<sub>2</sub>. A key focus of 20<sup>th</sup> century geomorphological work on karst became the climatic controls on the development of particular landforms and assemblages (Jennings, 1985), but there were typically few and generalized statements regarding implications for speleothems (e.g. Corbel, 1952). Bögli (1960) correctly emphasized the key control of organically-derived CO<sub>2</sub> in soils in driving more carbonate dissolution and stimulating more speleothem formation in tropical climates, but Trudgill (1985) cautioned that too much interpretation had been placed on CO<sub>2</sub> measurements of soil gas, and too little on transport processes.

**Figure 7.2:** (A) Conceptual model of the karst system with its physiology of water flow and CO<sub>2</sub> transport and release (Tooth, 2000). The upper part of the unsaturated zone (the epikarst), having both higher porosity and permeability, is an important source of stored water. (B) Cartoon of speleothem occurrence (black) in relation to cave sedimentational history (Smart and Francis, 1990). Remnants of an old wall-fill (I) probably pre-date sediment layer D as do the speleothem clasts within it. Unit C contains archaeological material and flowstones spreading out from the walls and incorporating breccia fragments. Unit B follows deposition of another flowstone and is then cut by a cave stream in which speleothems (F) have subsequently grown including a rimstone pool deposit (G) when the stream course was dammed. Speleothem unit A incorporates human remains and may continue to the present day. Percolating waters allowed local cementation (H), but the exact age is unclear. (C) The concept of karstic capture of high-resolution climatic signals (Fairchild, 2002). Annual temperature and rainfall variations are shown as the input, but longer-term changes are just as relevant. Likewise the examples of captured signals are in terms of trace element variations, but other suitable parameters include speleothem morphology, lamination or isotopic properties. In the trace element diagrams vertical bars spaced at annual intervals - Left, ultra-high resolution soda straw stalactite, Crag Cave, Ireland; right, more typical stalagmite record, Grotta di Ernesto, Italy - both modified from Fairchild *et al.* (2001).

An important starting point for modern geochemical studies of the carbonate system in cave waters is that of Holland *et*

*al.* (1964), who related water chemistry to host rock chemistry and cave processes and confirmed that CO<sub>2</sub>-degassing, rather than evaporation, was the key process stimulating speleothem formation. The importance of studies of dripwater hydrology and hydrogeochemistry (e.g. Pitty, 1966; Hendy and Wilson, 1968) is now firmly established (Baker *et al.*, 1999a; Fairchild *et al.*, 2000; Tooth and Fairchild, 2003; Musgrove and Banner, 2004; Mickler *et al.*, 2004), although carbonate system parameters have not always been included. The variation in CO<sub>2</sub> content of cave air, important in showcaves (e.g. Carrasco *et al.*, 2002), had less often been studied, but this is currently being rectified (Frisia *et al.*, 2000; Spötl *et al.*, 2005).



### 7.1.3 Other speleothem types and processes

This chapter does not cover caves in hydrothermal environments or soluble bedrocks where the bulk of the 255 recorded cave minerals are found (Hill and Forti, 1997). However, they provide some pointers to processes other than CO<sub>2</sub>-degassing that could be of potential importance. Slender eccentric twisted forms (helictites), typically associated with mineral coatings sealing cave walls, indicate evaporation in the cave environment (Hill and Forti, 1997). High levels of evaporation are typically associated with raised Mg/Ca in cave waters, and morphologically and mineralogically variable metastable carbonate precipitates. In evaporite host rocks, evaporation is the primary

mechanism of deposition, leading to a wide variety of recorded salts, of which gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is the most common.

A wide variety of minerals (particularly phosphates and organic minerals) are formed in caves with significant organic debris, but more subtly smaller amounts of such debris in the cave or overlying karst aquifer can give rise to additional fluxes of carbon dioxide to the cave environment. Intact pollen yields palaeoclimatic information (McGarry and Caseldine, 2004). Coatings of iron or manganese oxides are likely to indicate oxygen consumption in feeding waters, which may have impacts on speleothem chemistry.

Standing bodies of water produce characteristic phreatic growths of calcite crystals with well-developed crystal terminations, typically associated with rimstone dams (gour pools). Dating of such deposits points to varying water levels in the past (Fig. 7.1B), although there could be climatic (Bar-Matthews *et al.*, 2003) or hydrological causes for such variations. Cave rafts are precipitates forming at the surface of pools and can occur seasonally in response to higher rates of  $\text{CO}_2$ -degassing (Andreo *et al.*, 2002; Spötl *et al.*, 2005). Finally, significant air currents may be indicated by orientated speleothems, or by deposits identified as of aerosol origin (Hill and Forti, 1997). Speleothems can accumulate during prolonged periods of the history of caves and can be interrupted by episodes of clastic sedimentation (Sasowsky and Mylroie, 2004), by breakdown of deposits, sometimes induced by seismicity, and by archaeological disturbance. Figure 7.2B (after Smart and Francis, 1990) graphically illustrates the potentially complex stratigraphy.

#### 7.1.4 The capture of climatic signals in speleothems

Figure 7.2C presents the concept (Fairchild, 2002) of a climatic signal preserved in a speleothem, a signal that is mediated by the geomorphic and hydrologic environment, as discussed in detail in Fairchild *et al.* (2006a). Current research involves the forward modelling of processes that lead to the transformation of the input signal, and inverse modelling (Kaufmann and Dreybrodt, 2004) by appropriate transfer functions to recover aspects of the original climatic signal. However, progress is limited by the appropriate definition of system attributes as is illustrated in the next section.

### 7.2 Distribution, field occurrence and geomorphological/hydrological relations

#### 7.2.1 Ingredients for speleothem formation

Climate determines the timing and quantity of  $\text{H}_2\text{O}$  input, the degree to which it lies as snow, and to which it can potentially be recycled by evaporation. Climate (and the linked variables of altitude and topography) influences colonization by vegetation, whose development strongly affects the chemistry of the carbonate system and soil properties (facilitating speleogenesis), increases evapotranspiration, and is typically modified by human activity. The recharge of the aquifer with water (and the transport of  $\text{CO}_2$ , colloids and solutes in general) is strongly influenced by surface topography and the nature of soils and other surficial deposits as well as the degree and style of karstification of the aquifer. Karstic aquifers have a complex distribution of pore spaces including one-dimensional conduits, fractures, and “matrix” which facilitates mixing

and gives rise to a wide range of transmission times in the unsaturated zone. Although the conventional definition of speleothems only includes deposits in caves rather than smaller spaces (Hill and Forti, 1997), we need to be aware of processes outwith the caves (including deposition). Speleothems are typically fed by dripwaters with a large component of water derived from matrix storage, although faster flowpaths are relatively more important for flowstones. A crucial, somewhat neglected property is the nature of cave ventilation, which removes  $\text{CO}_2$  and allows speleothem formation to continue. In the following three sections we group the controlling factors to address the key issues of inflowing water quantity, water quality and in-cave processes.

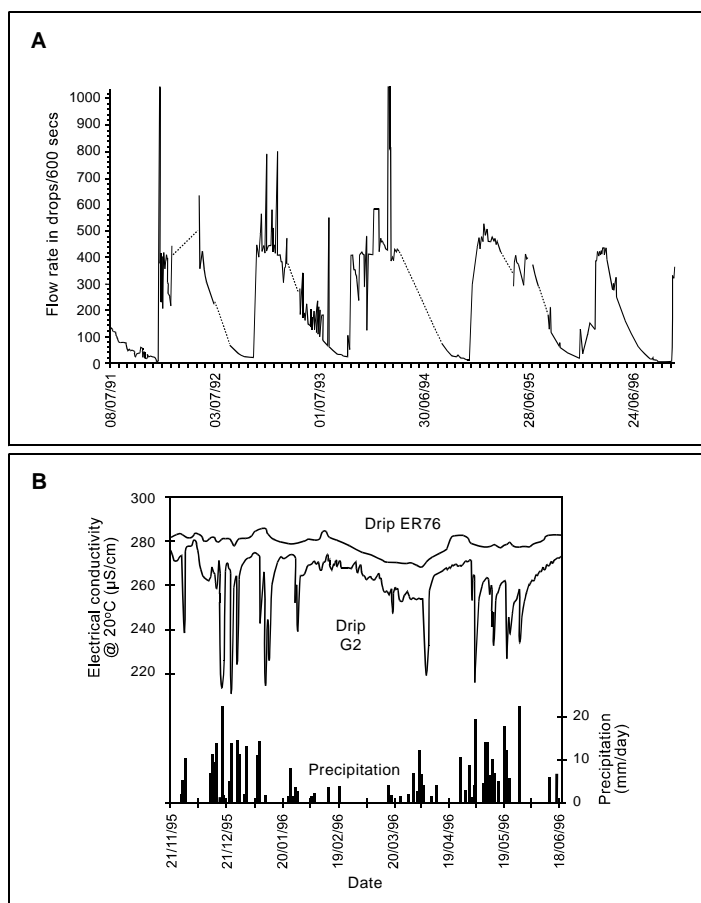
#### 7.2.2 Controls on quantity of speleothem-forming water inflow to caves

Climatic aridity clearly limits speleothem formation. However, speleothems are able to form even in semi-arid areas given sufficient infiltration from heavy rains and adequate storage capacity of the karstic aquifer. The timing of episodes of past speleothem growth in currently dry caves has proved extremely important in elucidating changes in atmospheric circulation (e.g. Burns *et al.*, 2001; Vaks *et al.*, 2003; Wang *et al.*, 2004).

Vegetation and animal activity in soils play important roles in generating macropores, which locally focus recharge into the karst aquifer (e.g. Beven and Germann, 1982; Tooth and Fairchild, 2003). A reduction in evapotranspiration by local deforestation could lead to an increase in seepage water in caves, which might be recognizable in palaeo-studies by carbon isotope evidence.

The aquifer structure causes a complex response to a water infiltration event. Recharge is focused into surface depressions (dolines) which are fed by lateral flow through a zone of enhanced permeability (the epikarst or subcutaneous zone) constituting the upper part of the karst aquifer. Dolines typically feed major conduits that are the primary channels of karst drainage. Speleothems are fed by a combination of seepage and fracture water, consistent with observations in quarried karstic aquifers indicating that the system consists of a matrix with a network of discontinuities (fractures or conduits). Models of complex aquifer behaviour (Smart and Friederich, 1986; Vaute *et al.*, 1997; Perrin *et al.*, 2003) are consistent with test results using artificial tracers (Bottrell and Atkinson, 1992), demonstrating dominantly vertical penetration with a range of flow-through times to drips in shallow caves ranging from days to over a year. Studies of frequently measured or automatically logged discharge (Smart and Friederich, 1986; Baker *et al.*, 1997a, Genty & Deflandre, 1998; Tooth and Fairchild, 2003; Baker and Brunsdon, 2003; Fairchild *et al.*, 2006b) illustrate the range of hydrological responses that can occur to infiltration events. Although fracture-fed flow normally results in flow increases, there can be local flow decrease (underflow) or non-linear behaviour, which relate to phenomena such as pockets of gas phase in the flow path, and hydrological thresholds in general. Seasonal-scale variations in drip rate are a feature of many climates (e.g. Fig. 7.3A, Genty and Deflandre, 1998). If a physically continuous water fill of cavities exists, pressure increases will be transmitted virtually instantaneously and so drip rates

are typically in phase with the seasonal variation in infiltration. Cases where they are out of phase (e.g. Nerja cave, Andreo *et al.*, 2002; Liñan *et al.*, 2002) perhaps reflect significant gas phase in the system.



**Figure 7.3:** (A) Seasonal variations in drip rate with superimposed short-term hydrological events from a stalactite in Pere-Nöel cave in Belgium; there is close relationship between flowrate and periods of high water excess (Genty and Deflandre, 1998). (B) Variations in cation loads, as monitored by electroconductivity, of dripwaters in response to seasonal patterns and individual infiltration events for two drips at Ernesto cave (Frisia *et al.*, 2000).

### 7.2.3 Controls on composition of inflowing waters

The greater abundance of speleothems in tropical climates is mirrored both by higher mean soil  $\text{PCO}_2$  at higher mean annual temperatures (Harmon *et al.*, 1975) and the positive relationship between growing season soil  $\text{PCO}_2$  and mean annual actual evapotranspiration (Brook *et al.*, 1983). These relationships arise because higher  $\text{PCO}_2$  waters can carry higher dissolved carbonate loads and hence can precipitate more when degassed (Fig. 7.4A). However, the data exhibit a large scatter and local controls can also be important in determining soil  $\text{PCO}_2$  (Miotke, 1974; Davis *et al.*, 2001; Tooth, 2000). Nevertheless, speleothem growth is inhibited in cooler climates, and distinct warmer periods of speleothem growth can be recognized in cool temperate regions during the late Quaternary (Baker *et al.*, 1993b).

Drake (1983), following Drake and Wigley (1975), attempted to explain data scatter with the important conceptual distinction of a “coincident system” (one in

which carbonate is dissolved to saturation at the  $\text{PCO}_2$  of the soil environment) versus a “sequential system” in which solutions discharging into the epikarst are undersaturated for  $\text{CaCO}_3$  (carbonate-poor soils) and reach saturation under conditions closed to re-supply of  $\text{CO}_2$ . Drake (1983) also cautioned against the notion of fixed seasonal values for soil  $\text{PCO}_2$  and water hardness; water dripping during high discharge events could be undersaturated, for example. Also, growth rate could be higher than expected for the climatic regime where, for example, high  $\text{PCO}_2$  and carbonate hardness arise from organic sources of  $\text{CO}_2$  within the epikarst, or where there is a source of strong acid, particularly sulphuric acid from pyrite oxidation (Atkinson, 1977, 1983; Spötl *et al.*, 2004).

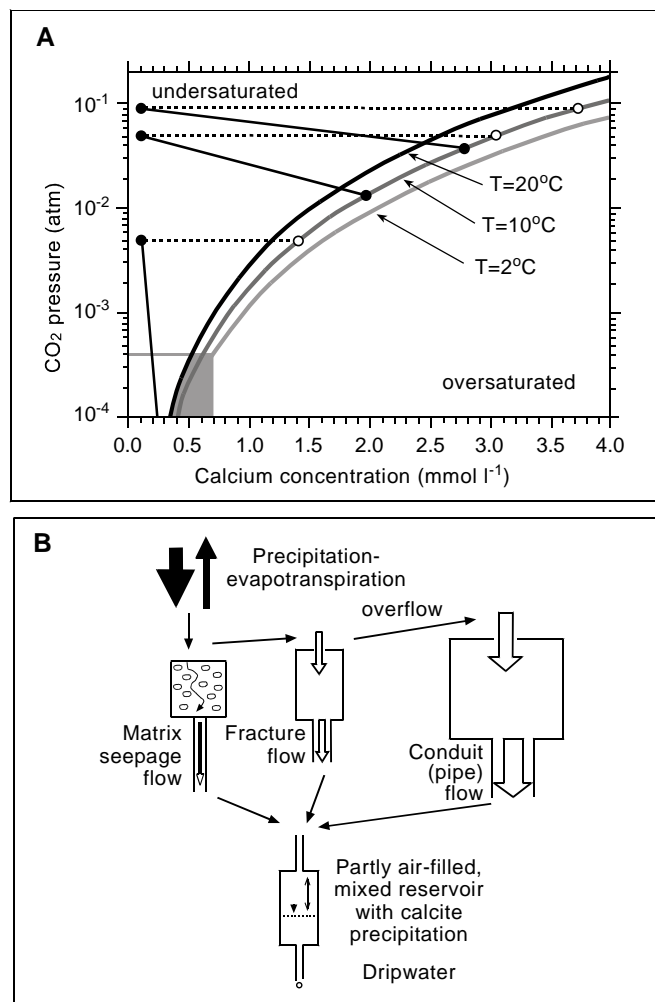
Earlier literature suggested that the seasonal pattern in  $\text{PCO}_2$  that is commonly found in karst soils is transmitted to the cave environment, leading to seasonal changes in water hardness and growth rate of speleothems (e.g. Moore, 1962; Gams, 1965; Pitty, 1966, 1968). This has been sufficiently influential as to form the starting point for explaining seasonal variations in the Ca content of cave waters (Genty *et al.*, 2001b). However, the original work did not demonstrate this phenomenon using conservative tracers, and most systems seem to behave differently: some, for example, are buffered by seasonally-invariant  $\text{CO}_2$  values in the epikarst (Atkinson, 1977; Fairchild *et al.*, 2000). Two other effects are more likely to lead to these changes. Firstly, a reduction in Ca content with only small changes in other cations is likely to be due to precipitation of  $\text{CaCO}_3$  up-flow of the drip site (Holland *et al.*, 1964). This was termed *prior precipitation* by Fairchild *et al.* (2000), who showed that it was enhanced during the dry season at Clamouse cave in southern France. The associated high Mg/Ca and Sr/Ca ratios have been used to develop an aridity index (McMillan *et al.*, 2005). Seasonally increased degassing occurs when drip rates are slow and the aquifer contains more gas spaces. Secondly, the  $\text{PCO}_2$  of cave air can be seasonally lowered as described in section 7.2.4.

Although the bulk of cations are derived by carbonate dissolution in soil and epikarst, carbon isotope studies indicate that the bulk of carbon is derived from organic sources: dripwaters and modern speleothems typically have 80-95% modern carbon (Genty *et al.*, 2001a). In Drake’s (1983) coincident system (open system of section 7.4.2), most dead carbon from aquifer dissolution diffuses out of the soil as  $\text{CO}_2$  into the atmosphere.

For other species, there can be significant contributions from marine aerosols and pollutants. The marine aerosol component of wet atmospheric deposition can be estimated from the chloride content of dripwaters, but pollution-related components are more difficult to determine directly. However, Frisia *et al.* (2005) demonstrated that trends in trace sulphate in speleothems can represent a record of atmospheric sulphur pollution. Comparison of rainfall with throughfall (via a vegetation canopy) illuminates some aspects of the vegetative flux. Leaching experiments or separation studies can isolate the contribution of aeolian or other allochthonous components of soils compared with the bedrock. The element most useful in sourcing studies is Sr, because sources often differ in their  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio and there is no fractionation of these isotopes during precipitation from



water. Speleothem time series in Tasmania (Goede *et al.*, 1998) reveal changes in carbonate aeolian input over time controlled by sea level and meteorological changes between glacial and inter-glacial conditions. Banner *et al.* (1996) and Verheyden *et al.* (2000) suggested that the differential rate of leaching from silicates (with high ratios) and carbonate (with low ratios) will lead to changes in dripwater and hence speleothem composition over time depending on the amount of rainfall.



**Figure 7.4:** (A) Dissolved Ca loads resulting from dissolution of pure limestone to saturation and their increase with (soil or epikarst) CO<sub>2</sub> (Fig.3 in Kaufmann, 2003). The horizontal data lines refer to “open” or coincident system dissolution whereby equilibrium with calcite is attained whilst still in contact with excess CO<sub>2</sub>. The “closed” or sequential system (lines sloping down to right) arises where water with a fixed CO<sub>2</sub> content subsequently reacts with CaCO<sub>3</sub> in the subsoil or karstic aquifer to reach equilibrium. (B) plumbing model illustrating processes affecting dripwater hydrology and hydrochemistry as used in Fairchild *et al.* (2006b).

There has been much interest in the use of trace elements as palaeoclimatic indicators, but early work underestimated the large variations in composition that occur between drips, depending on their flow path. Fairchild *et al.* (2000) found several mechanisms that would lead to enrichment in trace elements in or immediately following dry conditions: incongruent dissolution related to preferential retention of Ca

in soils due to freezing or evaporation; prior calcite precipitation; and enhanced dissolution of dolomite over long time periods (Roberts *et al.*, 1998). Since then, new data and modelling approaches (Baker *et al.*, 2000; Tooth and Fairchild, 2003; Fairchild *et al.*, 2006b) emphasise the importance, at low flow, of low-permeability seepage aquifer compartments, which are often enriched in particular trace elements (Fig. 7.4B).

The effects of infiltration events are quite variable spatially and range from an increase in flow with no change in chemistry in an entirely seepage-fed drip, to a rapid change in flow rate and composition in shallow fracture-fed sites (Tooth and Fairchild, 2003). Very rapid infiltration can be reflected in dilution of the water (Fig. 7.3B, Frisia *et al.*, 2000), although the opposite can be found in cases where the waters normally are saturated and a reduction in prior calcite precipitation (Fig. 7.4B) is the main consequence of the infiltration event (Fairchild *et al.*, 2006b). The introduction of soil-derived tracers (i.e. fluorescent humic and fulvic acids) is characteristic (Baker *et al.*, 1997a), and such colloids may even be associated with suspended sediment in extreme cases. Speleothem evidence at several European sites (Baker *et al.*, 1993b; Genty *et al.*, 1997; Proctor *et al.*, 2000; Frisia *et al.*, 2000; Huang *et al.*, 2001) suggests that the introduction of impurities can be largely confined to a brief interval in the autumn each year, perhaps reflecting a critical level of aquifer recharge at this phase of the hydrological year. This provides one of the key mechanisms for the development of annual properties of speleothems (as discussed in section 7.2.5).

#### 7.2.4 Cave factors that control the distribution and rate of growth of speleothems

The shape of cave passages influences the distribution of speleothems, but the rate of ventilation of caves in relation to the rate of input of fluids is also a critical control on speleothem growth. The development of cave passages is the subject of speleogenesis (see Klimchouk *et al.*, 2000). Caves can form below, at or above the water table, but the water table model is most relevant for tubular sub-horizontal cave passages that have the optimal shape for speleothem accumulation. Davis (1930) independently re-discovered the insight of Grund (1910, in Sweeting, 1981) that base level fall causes caves to evolve from a stage of active enlargement to a stage of filling with sediment and speleothems. Hence, the southern Chinese caves of the Guilin district (Sweeting, 1995) show progressively older, and better-decorated caves with increasing altitude. There are many examples in more complex environments where cave formation is multi-stage, and in any given case, there will be a strong control by rock structure, including both primary bedding and secondary features such as faults and joints.

Ventilation is a key parameter since a better-ventilated cave will have lowered PCO<sub>2</sub> and hence enhanced speleothem growth rates. A special case occurs when a cave stream dominates cave ventilation. Here, relative humidity will always be 100% and the cave air PCO<sub>2</sub> will be controlled by that of the stream, which can vary seasonally (Troester and White, 1984). More generally, the climate and geometry of the cave passages control ventilation. Although models of ventilation of caves with a large opening can be derived from

classical physics (Cigna, 1967; Wigley, 1967; Wigley and Brown, 1971, 1976), it is hard to derive the appropriate controlling parameters quantitatively even in systems with very simple geometry (Atkinson *et al.*, 1983; De Freitas and Littlejohn, 1987). Radon, derived from the  $^{238}\text{U}$  decay-series, is an effective tracer of circulation, and enhanced winter circulation, associated with lower Rn values, is commonly found (Hakl *et al.*, 1997; Dueñas *et al.*, 1999). Although ventilation is influenced by wind direction, the key control is a pressure difference between the cave interior and the external atmosphere in response to synoptic weather systems and the constant cave temperatures. This is most effective in chimney-type circulation where there are both upper and lower entrance points for air (Cigna, 1967; Wigley and Brown, 1976). Caves that descend from a single entrance will be expected to ventilate much more during the winter (Mavlyudov, 1997). Dramatic changes in  $\text{PCO}_2$  and  $\delta^{13}\text{C}$  or water and cave air in response to seasonal changes in ventilation have been demonstrated by detailed monitoring at the Austrian Obir cave (Spötl *et al.*, 2005). Our unpublished system calculations at the Ernesto cave suggest that day-to-day cave breathing is effective in regulating  $\text{CO}_2$  levels at this near-surface site, and the seasonal fall in  $\text{CO}_2$  (Frisia *et al.*, 2000; Huang *et al.*, 2001) could relate to a cut-off of epikarst gas supply by the seasonal filling of the aquifer with water. In both these sites, humidity remains very high, but in others, variations in humidity permitting seasonal evaporation may occur.

### 7.3 Macro- and micromorphological characteristics of flowstones, stalactites and stalagmites

#### 7.3.1 Flowstones

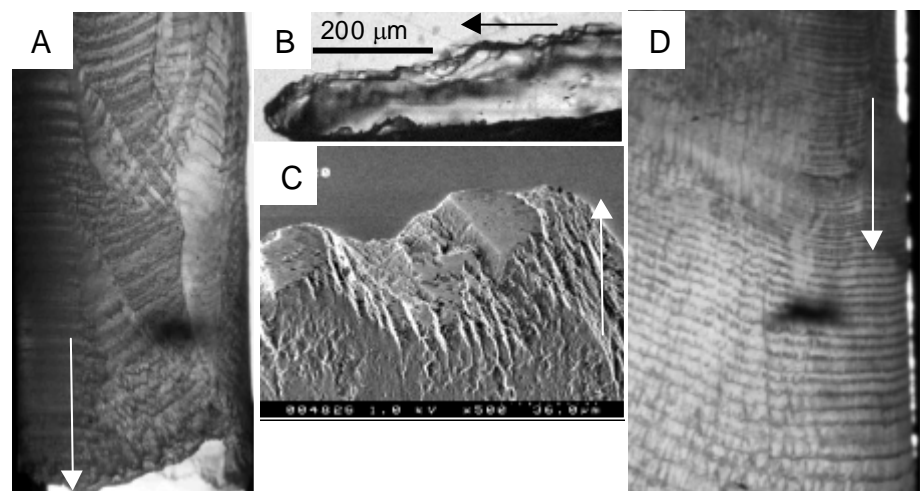
Flowstones (Fig. 7.1A) are widespread coverings of cave floor and walls that accrete roughly parallel to the host surface and may occur tens or hundreds of metres downstream of the water source (Ford and Williams, 1989). They have in common a tendency to display undulations in surface morphology and the lamina structure is dominantly parallel and continuous, but in detail there are many sub-types reflecting local slopes, water supply and other factors (Hill and Forti, 1997). Laminae arise primarily because of variations in impurity content and they may also fluoresce under ultraviolet excitation (Shopov, 2004). An advantage for palaeoenvironmental study is that flowstones can be cored with relatively little damage to the cave environment, and they can grow over tens of thousands of years. Conversely, there are issues of representativeness of a small core, and dating can be compromised by impurities. Flowstones often form under intermittent or weakly supersaturated thin flows of water and so typically accrete slowly (10–100  $\mu\text{m}/\text{year}$ ).

#### 7.3.2 Soda straws and other stalactites

Stalactites (Figs 7.1A,C and 7.5) and stalagmites (Fig. 7.1A, B, D and E) are related to dripping water and hence are called dripstones. Short *et al.* (2005) have applied a developed form of free boundary dynamics theory to predict the gravitationally-influenced conical shape of solid stalactites. The variable geometry of zones where water emerges then cause the variety of downward-growing forms

(Fig. 7.1C). For example, downwards-extending draperies or curtains develop along water trickle courses and can be translucent where crystal growth axes are perpendicular to their width (Ford and Williams, 1989). Some workers have cut solid stalactites to derive sections for successful palaeoclimatic work (Bar-Matthews *et al.*, 1999), but others have avoided them because of concerns over lamina geometry (Smart and Francis, 1990), or perhaps for fear of insufficient control on lateral changes in composition on their surface (Hendy, 1971).

Soda straw stalactites are hollow, with a diameter minimized by the surface tension of the water drop at their tip (Figs 7.1C and 7.5A, D; Curl, 1972). They have a wall only 0.1–0.4 mm thick (Fig. 7.5B), and so accrete primarily downwards with preferentially orientated crystals (Moore, 1962). Self and Hill (2003), drawing on the works of V.I. Stepanov and V.A. Maltsev, show that soda straws can continue to develop at the tip of solid stalactites (Fig. 7.1C) since water is drawn inside the soda straw only close to the tip. Soda straws drip relatively slowly, although the relationship to drip rates on solid stalactites has not been systematically investigated. Whilst soda straws can occur in dense inverted forests and sometimes break off under their own weight (Fig. 7.1A), they can extend up to several metres in length.



**Figure 7.5:** Soda straw stalactites from Ernesto cave (A, C, D) and Crag Cave (B) with arrows indicating direction of growth (originally downward). A and D are transmitted light views of the original straws which are 5 mm wide; B is a transmitted light view of a thick polished section through the stalactite wall and C is an SEM image. These stalactites show a thin calcite wall with a smooth exterior (base of image B) and a crystal-rough interior. The wall tapers to around 100  $\mu\text{m}$  wide at its tip (tip of arrow in A; left-hand side of B; top of C). The internal wall displays of myriad rhombic crystal terminations (B, C) with larger steps (tip of arrow in B; sub-horizontal lines in A and D) representing an annual rhythm of change of growth rate. The tip of the arrow in D represents the onset of faster growth at the end of the Little Ice Age in the 1860s.

Soda straw stalactites commonly display a lateral banding (Fig. 7.5A, D) whose regularity and spacing suggests an annual origin. First described by Moore (1962), this property is surprisingly unmentioned in later systematic

compilations. The banding sometimes reflects an undulating outer surface (Moore, 1962) and hence indicates external accretion, but far more commonly represents growth steps on the inner wall (Fig. 7.5B). A particularly neat way of confirming the annual origin of bands was found by Huang *et al.* (2001) who found equally-spaced internal impurity layers, homologous with layers in stalagmites from the same cave and known to be annual in origin (Frisia *et al.*, 2000). Soda straws consist of a few crystals that extend longitudinally downwards (Fig. 7.5A). Some have feathery, dendritic terminations (Self and Hill, 2003), which are said to “recrystallize”, or more likely be overgrown to form a more solid wall. More commonly, the wall tapers at the tip over the last year of growth (Fig. 7.5B). Crystal surfaces are covered with myriad rhombic terminations of crystallites that make up the macroscopic crystals (Fig. 7.5B, C). Although soda straws can be used to derive short, but unusually high-resolution proxy environmental records (Fairchild *et al.*, 2001), they are difficult to handle and analyze. A key point is that the banding, which is visible *in-situ* in the field when in the range of 0.1 to 1 mm spacing, points to a fundamental seasonality in the saturation state of karst waters, and hence the lateral rate of growth of the straws. This would otherwise take a large monitoring effort to uncover.

Baldini (2001) addressed the neglected issue of the relative volume of stalactites versus their underlying stalagmites, and found a correlation with drip rate that can be explained by the incomplete degassing of fast drips from soda straw stalactites (Moore, 1962). Rocques (1969, in Bögli, 1980) showed that CO<sub>2</sub>-degassing of droplets should be largely completed within a few minutes, although the rate of this process diminishes rapidly with time. This can be confirmed by the pH change that occurs following the placement of a drip from a soda straw on a suitable electrode. Conversely, it follows that where water has spent some time percolating on the outside of a solid stalactite, it should already be close to equilibrium with atmospheric CO<sub>2</sub>. Studies of pH of cave droplets ought to consider such issues more systematically in order to develop the ideas introduced by Baldini (2001).

### 7.3.3 Stalagmites: macromorphology

Stalagmite shape has attracted more systematic attention. Franke (1965) developed a theory of the control of stalagmite width by flow rate, with particular reference to cylindrical (candle) types (Fig. 7.1A, E). Curl (1973) also gave a theoretical justification for the minimum diameter of cylindrical forms (see also section 7.5.2). However, Gams (1981) showed that the width also increases with drip fall height because of splash effects. These effects tend to cause a change in morphology, with a sunken central splash cup developing (Bögli, 1980). A central depression can also arise by dissolution through periodic undersaturation of the drip water (Frisia, 1996). Franke (1965) mentioned other morphological types including those that have petal-like extensions from a cylindrical core, attributed to variations in growth rate and greater fall height (giving rise to splash effects). Franke (1965) referred also to conical forms in which there is significant growth on the sides of the structures (Fig. 7.1D, E): the morphology is attributed by him to a decreasing growth rate and by Gams (1981) to decreasing fall height as the stalagmite grows.

### 7.3.4 Stalagmites: fabric types

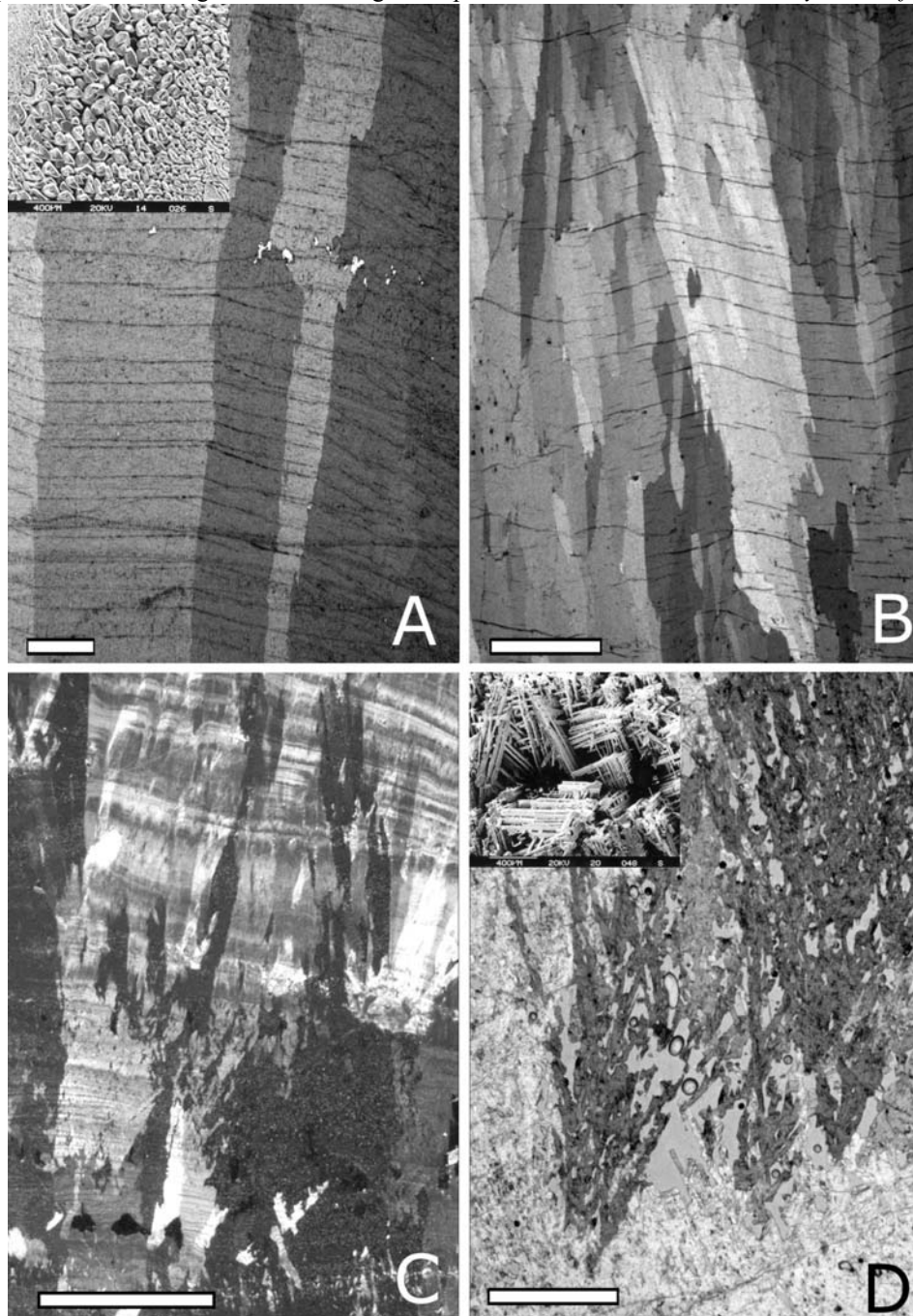
The internal composition of stalagmites may consist of either a single or several different fabrics. The term fabric, or texture, indicates the geometry and the spatial arrangement of single crystals that compose a synchronous layer (Grigor’ev 1961; Stepanov, 1997; Self and Hill, 2003). Speleothem crystal morphology is related to parent water flow and chemistry, in terms of drip rate and chemistry, capillary or gravitational supply of ions to growth sites, rate of CO<sub>2</sub> outgassing, and the variability of these factors (Gonzalez *et al.*, 1992; Genty, 1992; Jones & Kahle 1993; Kendall, 1993; Genty and Quinif, 1996). Ultimately, crystal morphology is generated by the dominant atomic growth mechanisms and so Frisia *et al.* (2000) included crystal microstructure when defining fabrics. A key concept was introduced by Kendall and Broughton (1978) who pointed out that stalagmite crystals are, in fact, composite-crystals formed by individual crystallites. Crystallites form separate terminations on the growth surface (e.g. inset in Fig. 7.6A and Fig. 7.7C), but have a minor space between them that is removed by lateral crystallite coalescence (overgrowth) just behind the growth front, or the space can remain as a fluid inclusion. Where speleothem surfaces are flooded, competitive growth fabrics occur, as in the model of Dickson (1993). In practice, the thin solution film (typically up to 100 µm) on the speleothem surface, limits the size of crystal units that can compete in this way (Broughton, 1983).

Kendall and Broughton (1978) drew on the BCF crystal growth model (Burton *et al.*, 1951). Consider a crystal made of building “blocks”: its surfaces could be smooth, if only one face of the each block is exposed at the surface, or show steps, when two faces of the blocks are exposed, or kinked, when three faces of the blocks are exposed. Step and kink sites are favourable for growth reactions and the number of such sites exposed to the surface may be increased when the density of crystal defects increases. Crystal defects may originate through, for example, the incorporation of foreign ions, misfits at impinging growth fronts, and condensation of vacancies (Wenk *et al.*, 1983), and commonly indicate either high growth rate or the availability of foreign ions or particles. Similar misfits could be caused by fluctuating flow rates, periodic exposure of the growing crystal faces to the cave air, rapid outgassing, or dissolution. In this light, Frisia *et al.* (2000) defined several fabric types as described below and shown in Fig. 7.6.

*Columnar fabric* (Fig. 7.6A, B) consists of crystals with a length to width ratio  $\leq 6$ , with usually straight crystal boundaries, uniform extinction and c-crystallographic axis perpendicular to the substrate. Crystals have a low density of crystal defects, the most common of which are dislocations. Where the length to width ratio is  $\geq 6:1$  the fabric is called fibrous (Folk, 1965). Its definition varies from that proposed by Kendall and Broughton (1978) because it includes the low density of defects which explains the ordered stacking of crystallites in each “composite crystal”, all of which have the same orientation with respect to the substrate. The crystallites that compose columnar fabric show flat faces at the solid-fluid interface. They commonly form through the spiral growth mechanism: the advance of monomolecular steps nucleated on screw dislocations. Columnar fabric commonly forms translucent stalagmites, and can show annual laminae, but whatever the cause of the lamination, it



does not perturb crystal growth. The fabric commonly forms at relatively low drip-water supersaturation and concentrations of foreign ions, and relatively constant flow conditions. Genty and Quinif (1996) distinguished porous and compact types of “palisadic” columnar fabric compact palisade fabric being indicative of higher drip rate.



**Figure 7.6:** Stalagmite calcite fabrics (all thin section photographs in crossed polars; scale bars = 2 mm). (A) Columnar fabric in CC4 from Crag Cave (Ireland). The straight features within crystals are cleavage planes. The upper box is a SEM micrograph showing the active stalagmite top, where the tips of crystallites composing the larger columnar individuals emerge. (B) Columnar fabric, from AL1, Grotta di Aladino (Italy). Note the irregular crystal boundaries and the cleavage planes. (C) Microcrystalline fabric from ER78, Grotta di Ernesto (Italy). Note the interfingered boundaries, intercrystalline porosity, growth laminae, nucleation sites, large voids (black in the

photograph), and the absence of cleavage planes. (D) Dendritic fabric in CC3 from Crag Cave (Ireland). The upper box is a SEM micrograph showing the scaffold-like arrangement of crystallites.

*Microcrystalline fabric* (Fig. 7.6C), not to be confused with the randomly orientated crystals of carbonate mud-micrite textures, has been discriminated from columnar fabric on the basis of the irregular stacking of crystallites and the high density of crystal defects. It has been observed in annually laminated alpine stalagmites, where it forms milky, opaque and porous layers. The misorientation of some crystallites with respect to their substrate yields composite crystals with serrated to interfingered boundaries, and patchy, rather than uniform, extinction. Crystallites are characterized by dislocations, repetitive twinning, and lamellae, indicative of high disturbance of the system related to flow variability and periodic input of growth inhibitors. Supersaturation does not seem to play an important role, because microcrystalline fabric forms at the same supersaturation conditions as columnar fabric.

*Dendritic fabric* (Fig. 7.6D) displays crystallites in branches similar to a dendrite crystal and its high density of crystal defects: twins, lamellae sub-grain boundaries and dislocations. The branching composite crystals are characterized by many macro-steps and macro-kinks, which can become new growth sites, thus explaining the scaffold-like appearance given by repetitive branching. It is a very porous fabric, typical of stalagmite formation under fluctuating discharge, strong outgassing phenomena, and periodic capillary flow.

*Fan fabric* is typical of aragonite, and it is formed by acicular (needle-like) or ray (with square termination) crystals radiating from a central nucleus. The

single aragonite crystals typically show micro-twinning (Frisia *et al.*, 2002).

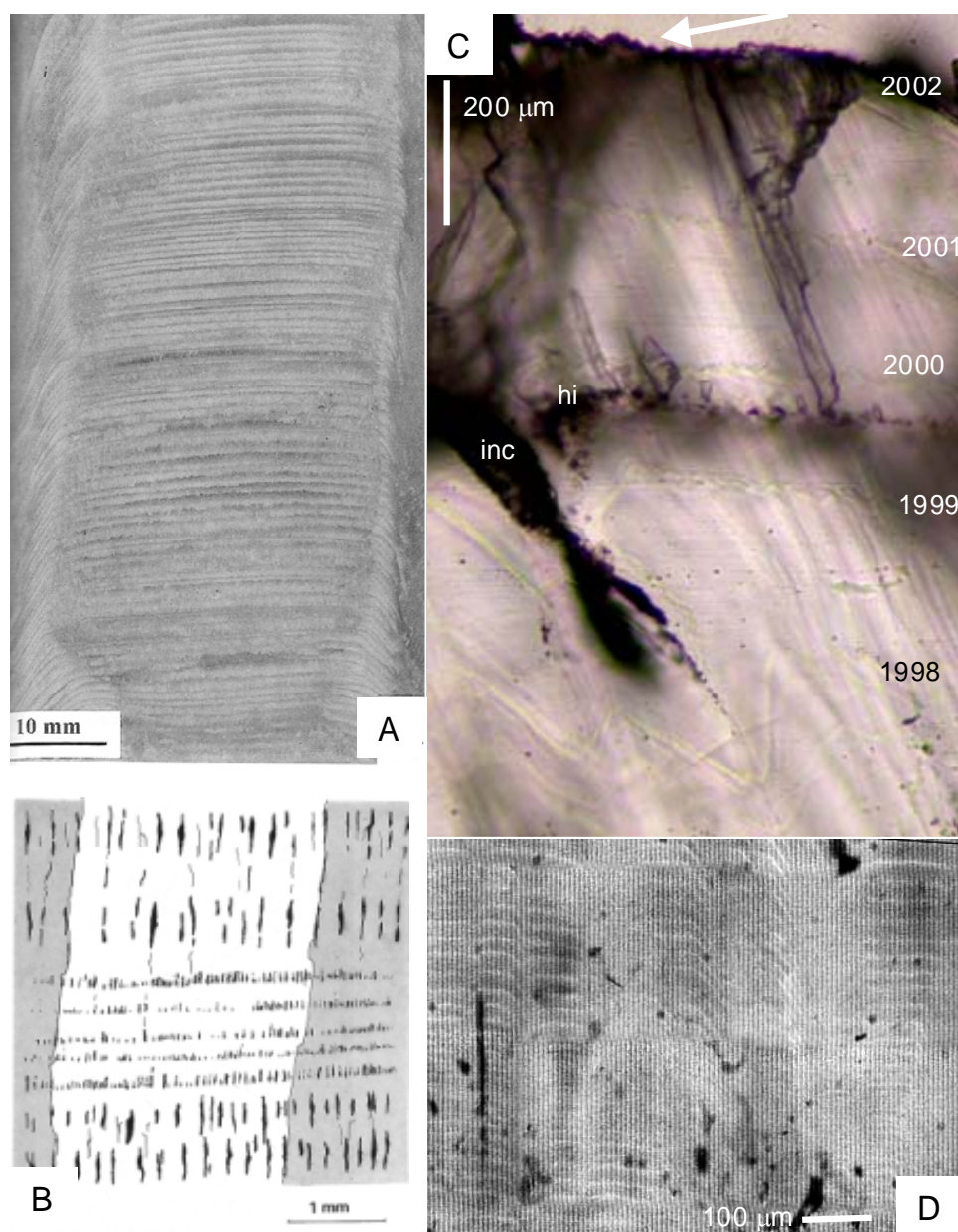
### 7.3.5 Stalagmites: annual lamination (couplets and organic-bearing laminae)

Sometimes, there is a repeated stacking of the fabrics (or laminae within fabrics) in an ordered succession, reflecting changes in the composition of the drip-waters. Two main types have been shown to occur on an annual scale: 1) seasonal alternations of fabric and/or mineralogy defining couplets, and 2) discrete pulses of impurities during infiltration events (Baker and Genty, 2003).

*Couplets* arise where there are seasonal variations in drip water composition and flowrate, leading to different crystal growth fabrics and chemistries. In settings with a pronounced dry season, deposition of two different phases of  $\text{CaCO}_3$  can occur. In a speleothem from Drotsky's cave in northwest Botswana, precipitation of calcite in the wet season, becoming progressively more Mg-rich over time, is followed by aragonite in the dry season (Railsback *et al.* 1994). In France and Belgium, Genty and Quinif (1996) and Genty *et al.* (1997) have recognized the typical occurrence of couplets of white porous calcite and dark compact calcite, resulting from seasonal variations in supersaturation and rate of dripping of supplying water (Fig. 7.7A, B), and Yadava *et al.* (2004) found similar couplets in aragonitic speleothems from India. Calcitic couplets occur in speleothems in the Guadalupe Mountains of New Mexico, where thin laminae represent dry conditions in time periods associated with archaeological evidence of cultural changes in indigenous peoples (Polyak and Asmerom, 2001). Perrette *et al.* (2005) show that there can be changes in the wavelength of UV fluorescence within presumed annual laminae, reflecting changing proportions of soil-derived humic and fulvic acids.

*Impurity pulse laminae* (Fig. 7.7C, D) typically have enhanced fluorescence under UV-excitation (Baker *et al.*, 1993b; Shopov *et al.*, 1994), reflecting enhanced input from soil. In some cases, the laminae are also clearly visible in thin sections in transmitted light (Fairchild *et al.*, 2001; Frisia *et al.*, 2003), or are primarily recognizable in this way. The existence of such laminae reflects a specific time of year when there is excessive infiltration, but their existence also relies on the hydrological functioning of the aquifer. The filling of the aquifer beyond a critical level may provide the mechanism for flushing of impurities through previously air-filled cavities at a specific stage in the hydrological year. This time in northwest Europe is mid-autumn. However, the annual origin of layering is not universal (Baker and Genty, 2003). For example, Baker *et al.* (1999b and 2002) describe the occurrence of doublets. Here, in specific years, two infiltration events occur and the second can be associated with snowmelt or an excessively wet period in the winter.

**Figure 7.7:** *Stalagmite laminae. A. and B, stalagmite PNst4, Père-Noël cave (from Genty and Quinif, 1996). (A) Polished hand specimen of stalagmite with flat-lying lamina*



*in core, and steeply-dipping laminae on flanks. Laminae are couplets: alternating white-porous and dark-compact layers. (B) section of thin section illustrating that the white-porous laminae represent trains of inclusions; laminae are much thinner, and the inclusions smaller, in the central area; crystals differentiated by shading. (C) Stalagmite sample Obi 84, from Obir Cave, SE Austria (sample of Prof. C. Spötl). The sample was collected in December 2002. Narrow autumnal laminae show zig-zag terminations of crystallites. The crystallite boundaries are aligned NNW-SSE in the image and crystallite terminations at the top surface are arrowed. The 1998 lamina displays high-relief which appears to presage the incorporation of an air inclusion (labelled inc) and this lamina also is a doublet. Within the 2000 lamina there is a growth hiatus (laterally discontinuous outside the field of view), labelled "hi" corresponding to a line of fluid inclusions and the development of some calcite nuclei with different optical orientations. (D) Part of a photomosaic produced by Dr. C. Proctor of UV-fluorescence of sample SU96-7 from Tartair cave, NW Scotland (Proctor *et al.*, 2002; Fairchild *et al.*, 2001). Narrow vertical lines are imaging artefacts and black areas are fluid inclusions. The narrow fluorescent laminae reveal parallel growth of calcite crystallites.*

## 7.4 Chemistry of speleothems

### 7.4.1 Dating methods

Whereas interval dating can be carried out by counting annual layers (e.g. Baldini *et al.*, 2002), radiometric techniques are needed to provide the overall time constraints on long-term speleothem deposition. The most widely applicable radiometric technique is  $^{230}\text{Th}$ - $^{234}\text{U}$ - $^{238}\text{U}$  disequilibrium dating, which can be used between a few hundred years (limited by determination of  $^{230}\text{Th}$ ) to around 500 ka (Edwards *et al.*, 1987). Uranium is incorporated into  $\text{CaCO}_3$  as the uranyl ion  $\text{UO}_2^{2+}$ , derived from the dominant aqueous species ( $\text{UO}_2(\text{CO}_3)_3^{4-}$ ), whereas Th is practically insoluble and so will be incorporated into speleothems only with non-carbonate phases. Contamination by Th offers analytical challenges, but these can be overcome with sufficient knowledge of primary  $^{230}\text{Th}$ / $^{232}\text{Th}$  ratios (Richards and Dorale, 2003). Precision is limited by primary U concentration, which is variable over several orders of magnitude. U is enriched in aragonite compared with calcite, due to its favourable coordination environment (Reeder *et al.*, 2000). The rapid technological evolution during the last 20 years from alpha-spectrometry to thermal ionization mass spectrometry (TIMS) (Edwards, *et al.*, 1987) and to multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) dramatically increased the resolution and the precision of the dating system. The sample size decreased from 10-100 grams ( $\alpha$ -spectrometry) to 10-500 mg (TIMS and MC-ICPMS), and the precision ( $2\sigma$ ) in the  $^{230}\text{Th}$  analyses ameliorated from 2-10% to 0.1-0.4% (Goldstein & Stirling, 2003). In addition to dating issues,  $^{234}\text{U}/^{238}\text{U}$  ratio variations have also proved useful as palaeohydrological proxies (Ayalon *et al.*, 1999; Frumkin and Stein, 2004).

U-series dating of speleothems has played a significant part in Quaternary science in recent years. A significant geomorphological application is the estimation of rates of denudation of the landscape (Atkinson and Rowe, 1992). The groundwater-fissure deposit at Devil's Hole, Nevada, which grew for 0.5 Ma (Winograd *et al.* (1992), showed some discrepant dates of inferred glacial terminations compared with Milankovitch theory. Glacial termination II also occurred earlier than predicted from Milankovitch theory in a climatically sensitive Alpine site (Spötl *et al.*, 2002, 2004), although this is not the case in China (Yuan *et al.*, 2004). The ages of the Dansgaard-Oeschger events during the last glacial cycle have been most accurately determined using speleothems (e.g. Spötl and Mangini, 2002; Genty *et al.*, 2003). Finally, data from submerged Bahamian speleothems have been used to extend the calibration of the  $^{14}\text{C}$  timescale (Beck *et al.*, 2001).

Other dating techniques include different isotopes from the Uranium decay series. In particular,  $^{231}\text{Pa}$ - $^{235}\text{U}$  can be applied within the 0-200 ka time span (Edwards *et al.*, 1997), while U-Pb dating can be used for old speleothems with high U content and low Pb (Richards *et al.*, 1998), but applications have been limited to date. For samples older than 500 ka, low-precision ages can be obtained from palaeomagnetic methods, electron-spin resonance (Grün, 1989) and  $^{234}\text{U}/^{238}\text{U}$  disequilibrium (Ludwig *et al.*, 1992). For young samples,  $^{14}\text{C}$ -dating was used before U-series dating became firmly established, but is limited by

uncertainty over the percentage of dead carbon in a given sample incorporated during growth (Genty *et al.*, 2001a).

### 7.4.2 Stable isotope composition

Stable isotope studies have formed the major type of geochemical investigation of speleothems (Harmon *et al.*, 2004; McDermott, 2004). Such work was stimulated initially by the prospect of palaeotemperature analysis, given that cave interiors usually approximate the mean annual external temperature (variations with depth are discussed by Leutscher and Jeannin, 2004). The oxygen isotopic composition of calcium carbonate ( $\delta^{18}\text{O}_\text{c}$ ), formed in isotopic equilibrium with a water of fixed composition ( $\delta^{18}\text{O}_\text{w}$ ), decreases with increasing temperature. However, it is now recognized that changes in the water composition form the main agent for change in  $\delta^{18}\text{O}_\text{c}$  over time, and so one current research focus is the technically challenging extraction of coeval water from fluid inclusions to determine the  $\delta^{18}\text{O}_\text{w}$  composition directly, or via the meteoric water line, from  $\delta\text{D}$  (Matthews *et al.*, 2000; Dennis *et al.*, 2001; McGarry *et al.*, 2004).

In most cave systems, equilibrium isotopic fractionation is modified by kinetic effects (Mickler *et al.*, 2004) resulting from factors such as high supersaturation of the water (Kim and O'Neil, 1997), and outgassing and evaporation (Gonzalez and Lohmann, 1988). Fortunately, cave carbonates often form in quasi-isotopic equilibrium, that is from waters at relatively low supersaturation, constant drip rate, and cave relative humidity of circa 100%. The only calcite fabric normally associated with strong kinetic isotope fractionations is dendritic fabric, in the case of carbon isotopes. Aragonite is slightly heavier in needle crystals compared to fibres (Frisia *et al.*, 2002).

Where only limited evaporation occurs at the surface or in the epikarst, the mean isotopic composition ( $\delta^{18}\text{O}_\text{w}$ ) of cave drip-waters reflects the mean annual isotopic composition of precipitation ( $\delta^{18}\text{O}_\text{p}$ , Yonge *et al.*, 1985). In regions with semi-arid or arid climate, evaporative processes lead to heavier  $\delta^{18}\text{O}_\text{w}$  values than precipitation (Bar-Matthews *et al.*, 1996). In principle, different parts of the aquifer could preferentially store isotopically distinct water from different seasons. Although not necessarily significant (McDermott *et al.*, 1999), the site-specific nature of this issue makes modern monitoring studies advisable.

The oxygen isotope composition of atmospheric precipitation ( $\delta^{18}\text{O}_\text{p}$ ) becomes increasingly negative with decreasing temperature due to progressive removal of vapour in a Rayleigh fractionation process, but changes in water source characteristics render the temperature dependence of  $\delta^{18}\text{O}_\text{p}$  variable and site-dependent. For mid- to high-latitude regions, the  $\delta^{18}\text{O}_\text{p}$  dependence on temperature averages  $+0.59 \pm 0.09$  ‰ per °C (Dansgaard, 1964; Rozanski *et al.*, 1993). This positive dependence exceeds the calculated calcite-water fractionation at equilibrium (about  $-0.24$ ‰ per °C). As temperature usually has a larger effect on the  $\delta^{18}\text{O}_\text{p}$  than on the calcite-water fractionation, a positive correlation between temperature and  $\delta^{18}\text{O}_\text{c}$  should be expected in many mid- and high-latitude sites. Heavier  $\delta^{18}\text{O}_\text{c}$  has thus been taken to reflect warmer mean annual temperatures (Dorale *et al.*, 1992, 1998; Gascoyne, 1992; McDermott *et al.*, 1999,



2001; Paulsen *et al.*, 2003). The tenability of the approach must, however, be tested for each site; for example the opposite relationship in north Norway was found by Lauritzen and Lundberg (1999).

In many regions, it has been observed that the most intense rainfall have the lowest  $\delta^{18}\text{O}_p$ . Thus, in rainy periods or seasons the  $\delta^{18}\text{O}_c$  would reflect this “amount effect” on  $\delta^{18}\text{O}_p$ . This has been observed in monsoon regions, where the most depleted  $\delta^{18}\text{O}_c$  values correspond to heavier monsoon rain intensity (Fleitmann *et al.*, 2003). A high correlation between high-resolution (annual)  $\delta^{18}\text{O}_c$  series from Oman speleothems and the residual  $^{14}\text{C}$  ( $\Delta^{14}\text{C}$ ), provided well-constrained evidence of solar activity influence on the Indian Ocean monsoon (Neff *et al.*, 2001; Fleitmann *et al.*, 2003). A similar correlation has been demonstrated also in continental humid settings (Niggeman *et al.*, 2003), and can be interpreted as solar forcing effects on European storm tracks (Shindell *et al.*, 2001). Thus, the  $\delta^{18}\text{O}_c$  of speleothems is a powerful tool to detect solar forcing effects. Caves in Israel have been particularly well calibrated for the influences of rainfall amount and source effects on  $\delta^{18}\text{O}_c$  (Bar-Matthews *et al.*, 1996, 1999, 2000; Kolodny *et al.*, 2003).

The equilibrium carbon isotope composition of aragonite is around 2 ‰ greater in aragonite than calcite, but aragonite is typically slightly heavier than expected because of kinetic effects (Frisia *et al.*, 2002). Where calcite later replaces the thermodynamically unstable aragonite, it can preserve evidence of the original heavier  $\delta^{13}\text{C}$  aragonite composition (Frisia *et al.*, 2002). The carbon isotopic composition of cave carbonates ( $\delta^{13}\text{C}_c$ ) depends on the  $\delta^{13}\text{C}$  composition of the dissolved inorganic carbon (DIC), on growth rate (Turner, 1982), on changes with the gaseous phase and the supersaturation state of the water with respect to calcium carbonate (Richards and Dorale, 2003). As for the case of oxygen, the carbon isotopic composition of the parent water seems to be in many cases the most important factor determining the  $\delta^{13}\text{C}_c$  of speleothem carbonates. The carbon dissolved in drip waters mainly derives from three sources: atmospheric  $\text{CO}_2$ , soil  $\text{CO}_2$  and dissolution of the karstic host rock. Variations in the isotopic composition of soil  $\text{PCO}_2$  have been held to be important (Denniston *et al.*, 2000; Frappier *et al.*, 2002; Paulsen *et al.*, 2003; Genty *et al.*, 2003). For example, the  $\delta^{13}\text{C}$  composition of soil  $\text{CO}_2$  varies according to the photosynthetic pathway of plants. The  $\delta^{13}\text{C}$  values of respired soil  $\text{CO}_2$  of C3 trees and shrubs adapted to a relatively cold and wet climate typically range between –26 and –20 ‰, and those of C4-type drought-adapted grasses range between –16 and –10‰ (Cerling, 1984). The control on  $\delta^{13}\text{C}$  by a change in type of photosynthetic pathway is well illustrated by studies in the American mid-west (e.g. Dorale *et al.*, 1998). Under dry conditions, however, the  $\delta^{13}\text{C}$  of respired soil  $\text{CO}_2$  of C3 plants becomes heavier due to restricted stomatal conductance (Paulsen *et al.*, 2003), and under humid conditions it is lighter. Thus, given that all other environmental conditions are the same, the  $\delta^{13}\text{C}_c$  of cave carbonates should be lighter when the vegetation above the cave mostly consists of C3 plants living under unlimited water availability conditions, and heavier when the vegetation consists of C4 plants, or under arid settings.

Genty *et al.* (2003) also indicate that cool climates inhibit soil  $\text{CO}_2$  production and yield heavier  $\delta^{13}\text{C}_c$ .

The  $\delta^{13}\text{C}_c$  values become heavier also in case of within-cave phenomena, mostly related to outgassing (Baker *et al.*, 1997b). At equilibrium,  $\delta^{13}\text{C}$  of DIC is isotopically heavier by around 10 ‰ compared with gaseous  $\text{CO}_2$ . Hence, speleothem calcite deposited in ventilated cave passages are likely to be characterized by heavier  $\delta^{13}\text{C}_c$  than speleothem calcite formed in secluded, non-ventilated passages, and supersaturations are likely to be higher, leading to disequilibrium fabrics. Calcite fabrics developed under disequilibrium conditions, such as the dendritic fabric, show  $^{13}\text{C}$  enrichment with respect to the columnar fabric (Frisia *et al.*, 2000). Equilibrium fractionation modelled as a progressive Rayleigh distillation process was able to account well for the variations in  $\delta^{13}\text{C}$  of dripwaters in Soreq cave (Bar-Matthews *et al.*, 1996). Additional kinetic effects due to fast degassing could also occur (Hendy, 1971) and Spötl *et al.* (2005) showed that kinetic enhancement of carbon isotope fractionation becomes important in strongly ventilated cave passages.

#### 7.4.3 Trace element compositions and their controls

Controls on the water composition were discussed in section 7.2.3, but additional complexities arise by the partitioning of species into  $\text{CaCO}_3$ . In principle, three groups of elements or species can be distinguished:

(a) those that substitute for Ca or  $\text{CO}_3$  in the  $\text{CaCO}_3$  lattice (e.g. Sr, Ba and U in aragonite and calcite, and Mg and  $\text{SO}_4$  in calcite). Here a partition coefficient (K) may be defined:  $\text{Tr}/\text{Cr}_{\text{CaCO}_3} = K * \text{Tr}/\text{Cr}_{\text{solution}}$ , where Tr is the trace element or species and Cr is the carrier Ca or  $\text{CO}_3$ . K varies with mineral species and may vary with temperature, growth kinetics or other factors (Morse and Bender, 1990). It is also dependent on the crystallographic form, which may account for the complex geochemical zoning in aragonites recorded by Finch *et al.*, (2001, 2003). For calcite, partition coefficients apply to rhombohedral crystals (Huang and Fairchild, 2001), and the values represent a mean of the two forms of incorporation at antipathetic growth steps as observed in experimental products (Paquette and Reeder, 1995).

(b) those that are incorporated interstitially on a molecular scale in  $\text{CaCO}_3$  (e.g.  $\text{PO}_4$ , Na and F in calcite). Typically these components are preferentially incorporated at growth defects and so tend to be more abundant where crystals have more defects, related to either rate or style of growth. Hydrogen, as measured by ion probe (Fairchild *et al.*, 2001), probably reflects either molecular water or fluid nano-inclusions.

(c) those that are present in fluid or solid inclusions within the  $\text{CaCO}_3$ . In cases where solid inclusions are brought in by high flows, the distribution of such elements could be hydrologically significant.

Finch *et al.* (2003) and Treble *et al.* (2003) have been able to derive empirical transfer functions for rainfall in South African and west Australian examples, by comparison of data from selected trace elements (mostly in the first group)

with instrumental climatic data. McMillan *et al.* (2005) showed that annual trace element trends in stalagmites from Clamouse cave follow those expected from seasonal dryness and that they are superimposed on a long period of relative drought 1100-1200 years BP. Hellstrom and McCulloch (2000) emphasised the utility of combined trace element and isotopic data in palaeoclimatic studies.

Annual variations in trace elements are now known to be a normal feature of caves in shallow karst environments (Roberts *et al.*, 1998; Finch *et al.*, 2001; Huang *et al.*, 2001; Fairchild *et al.*, 2001, Fairchild, 2002) and sub-annual variations can also be observed where speleothems grow sufficiently quickly. These variations can be related mainly either to changes in the ion ratios in solution in relation to hydrological effects, or to seasonal changes in supersaturation of karst waters, that is the same two controls that are responsible for petrographic laminae. In section 7.6.2, such variations are related to potential controlling factors.

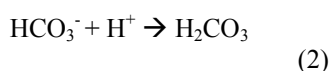
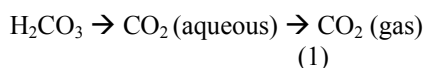
#### 7.4.4. Organic geochemistry

Total organic carbon measurements have also been used (Batiot *et al.*, 2003) to trace karstic hydrology, but the UV-fluorescing fraction (e.g. Baker and Genty, 1999; Baker *et al.*, 1999a) appears to be selectively incorporated in speleothems (McGarry and Baker, 2000). Relatively little molecular organic geochemistry has been carried out. Lauritzen *et al.* (1994) made a pioneering study of long-term records of amino acid racemization and there is currently interest in assessing the environmental associations of different types of organic molecule. For example, Xie *et al.* (2003) demonstrated changes in the relative incorporation of low and high molecular weight lipids that correlated with trends in  $\delta^{13}\text{C}$ . Given also increasing evidence for the involvement of microbial films in  $\text{CaCO}_3$  precipitation on speleothems (e.g. Cacchio *et al.* [2004], who show that different bacterial strains generate precipitates of differing  $\delta^{13}\text{C}$  composition), this will be a rich field for the future.

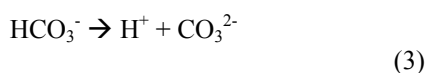
### 7.5 Mechanisms of formation

#### 7.5.1 The $\text{CO}_2$ -degassing model and its consequence for speleothem growth rate

In general, more highly supersaturated solutions will tend to precipitate  $\text{CaCO}_3$  more quickly. Supersaturation arises by a set of reactions, which involve a loss of volatile acid (carbon dioxide) from the solution:



Because the last reaction reduces  $\text{H}^+$  proportionally much more than  $\text{HCO}_3^-$ , it stimulates the following reaction:



The increase in carbonate ( $\text{CO}_3^{2-}$ ) ion raises the saturation state of the solution as defined by the saturation index for calcite ( $\text{SI}_{\text{cc}}$ ), where:  $\text{SI}_{\text{cc}} = \log(\text{IAP}/K_s)$  where IAP (ionic activity product) =  $(\text{Ca}^{2+})(\text{CO}_3^{2-})$  in a given solution and  $K_s$

is the solubility product. Where the IAP and  $K_s$  are equal,  $\text{SI}_{\text{cc}}$  is zero and the solution is at equilibrium with calcite; positive values of  $\text{SI}_{\text{cc}}$  correspond to supersaturation. Growth may be inhibited if  $\text{SI}_{\text{cc}} < 0.05$ -0.15, or if there are species in solution which block growth sites.  $\text{SI}_{\text{cc}}$  values rarely exceed 0.5-0.7 in caves, but commonly approach 1 in surface karst streams where degassing is rapid (Dandurand *et al.*, 1982). Extremely high growth rates also occur where speleothem growth is sourced from hyper-alkaline waters flowing through concrete structures or lime kilns (Moore, 1962), but here the controlling reactions are different (Baker *et al.*, 1999b).

The most fundamental advances in our understanding of the physical controls on growth rate of calcite have come from the work of Dreybrodt and co-workers, as summarized in Dreybrodt (1988, 1999), Baker *et al.* (1998) and Kaufmann (2003). The rate of growth (R) thus depends on both the cationic and anionic behaviour in the system, but in many cases can be simplified to be a function of Ca concentration, as follows:

$$R = \alpha (c - c_{\text{eq}})$$

where  $\alpha$  is a rate constant (units of  $\text{cm s}^{-1}$ ),  $c$  is the Ca concentration ( $\text{mol L}^{-1}$ ) in the solution, and  $c_{\text{eq}}$  is the Ca concentration at equilibrium with calcite. Kaufmann (2003), following Dreybrodt (1999), substitutes  $c_{\text{eff}}$  for  $c_{\text{eq}}$  where  $c_{\text{eff}}$  is the effective equilibrium value allowing for kinetic inhibition and equates to a  $\text{SI}_{\text{cc}}$  value of around 0.05. Values of  $\alpha$  depend on temperature and the  $\text{PCO}_2$  of the cave air.

The analysis considers the simultaneous operation of three processes, each of which could limit growth rate under particular circumstances:

(a) Reactions at the surface of the calcite crystal. These are given by the PWP model of Plummer *et al.* (1978), which applies also to calcite dissolution. These reactions are rate-limiting where the solution is only weakly supersaturated.

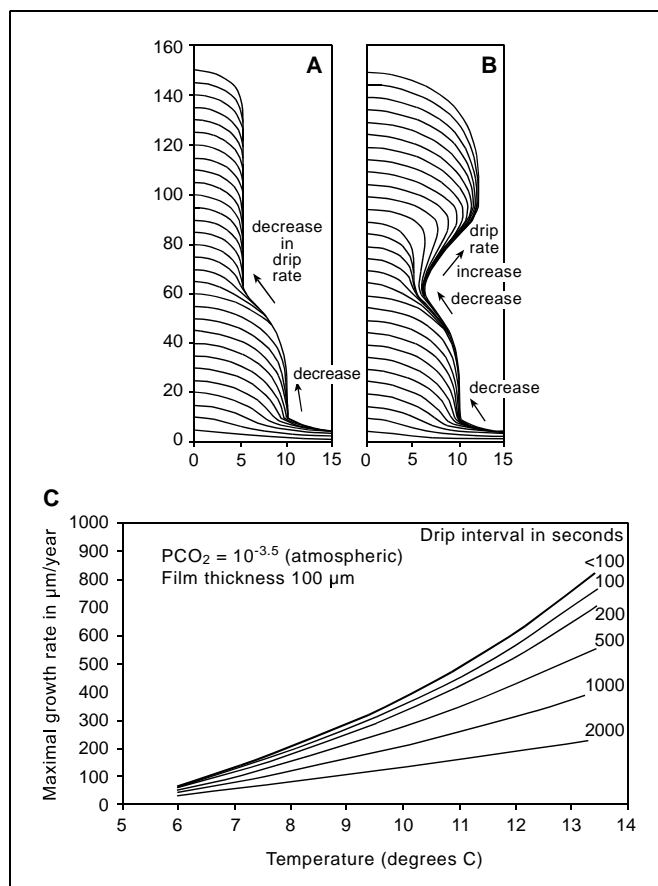
(b) As a result of  $\text{CaCO}_3$  precipitation,  $\text{CO}_3^{2-}$  ions are consumed which drives reactions (3), (2) and (1) as above and results in  $\text{CO}_2$ -degassing, in addition to that which will have been occurring in any case if the solution had not had time to reach equilibrium with the cave atmosphere (solution  $\text{PCO}_2 >$  cave atmospheric  $\text{PCO}_2$ ). The process of  $\text{CO}_2$ -formation becomes rate-limiting if the film of water between the calcite surface and the cave atmosphere is very thin, and diminishes up to film thickness of 200  $\mu\text{m}$ . Most speleothems have film thicknesses within this range.

(c) Mass transport of species away from the growing calcite surface. This becomes important at fast growth rates or when there is a thick stagnant film of water ( $> 400 \mu\text{m}$ ), as in gour pools, or small depressions on flowstone or stalagmite surfaces.

Baker and Smart (1995), Baker *et al.* (1998) and Genty *et al.* (2001b) have carried out the most extensive field-tests of the Dreybrodt growth model in cave environments and have found generally good agreement within a factor of 2 for



stalagmites, with somewhat more variability for flowstones. Genty *et al.* (2001b) have provided the first extensive analysis of seasonal variations in growth rate in relation to Ca concentrations, which in most cases bear a relationship to depositional temperature.



**Figure 7.8:** (A, B) Examples of modelled speleothem macro-morphologies of speleothems illustrating the concept of equilibrium shapes developed by constant rates of vertical accretion, but modified by changing drip rate, where the diameter is a positive function of driprate (Dreybrodt, 1999, Fig. 3). The equilibrium radius in cm is given by  $(V/\pi \alpha \Delta T)^{0.5}$  where  $\Delta T$  is the time interval between drips,  $V$  is the drip volume and  $\alpha$  is the growth rate constant as introduced in section 7.5.1. (C) Modelled maximal growth rates of speleothems under a stagnant fluid layer by combining the predictions of the Dreybrodt growth model with the field data on Ca concentration of dripwaters in Genty *et al.* (2001). Factors such as prior calcite precipitation are known to have reduced Ca (Fairchild *et al.*, 2000; 2005) at certain of the sites of Genty *et al.* (2001b), so their linear regression line is modified to rise from 50 mg/litre at 6 °C to 160 mg/litre at 14 °C. Reasons for growth rates to lie below these maximal values are discussed in the text.

In Fig. 7.8C, we combine the algorithms expressing the Dreybrodt model given in Baker *et al.* (1998) and Kaufmann (2003) with the field data on the variation of  $\text{Ca}^{2+}$  content of dripwaters with cave temperature given by Genty *et al.* (2001b), to express the maximal growth rates expected with temperature at different sites. The growth rates could be even faster with film thickness of 200-400  $\mu\text{m}$ , but such thicknesses are not typical. Growth rates around the

maximal level are found, for example, at the Ernesto cave today (Frisia *et al.*, 2003) at 6.5 °C. However there are several reasons why non-porous speleothems fail to grow this fast:

(a) the film thickness may be thinner. At 50  $\mu\text{m}$  thickness and 10 °C using the conditions of Fig. 7.8C, the growth rate reduces by about one-third.

(b) the initial Ca concentration of cave water might be limited by lower-than-expected soil  $\text{PCO}_2$  because of relative aridity (Genty *et al.*, 2001b) or where the solutions follow a sequential evolution (Drake, 1983) and reach saturation at lower  $\text{PCO}_2$  values than the soil.

(c) the cave may be insufficiently ventilated. If  $\text{PCO}_2$  is ten times atmospheric, the growth rate diminishes by around 25% (or rather more at lowered Ca concentrations such as if factors 2 or 4 apply – see Fig. 3 in Baker *et al.*, 1998). When more seasonal cave  $\text{PCO}_2$  data (e.g. Huang *et al.*, 2001; Spötl *et al.*, 2005) become available, the effects of seasonally enhanced ventilation can be added to the approach of Genty *et al.* (2001b).

(d) prior calcite precipitation may already have occurred. This must be a major factor for drips falling from active solid stalactites and it has tended to be underestimated in the past.

(e) the drip rate is slow so that growth is limited by the supply of fresh, supersaturated solution (see lower lines on Fig. 7.8C). An example of this effect is the correlation between thickness of calcitic laminae and rainfall in Drotsky's Cave, Botswana (Railsback *et al.*, 1994), where the calcite layers alternate with aragonite layers formed in the dry season. Generally, at very slow drip rates, it becomes more likely that evaporative effects also come into play. Even in the more humid climate of Belgium, Genty and Quinif (1996) found a good correlation between water excess and thickness of annual laminae.

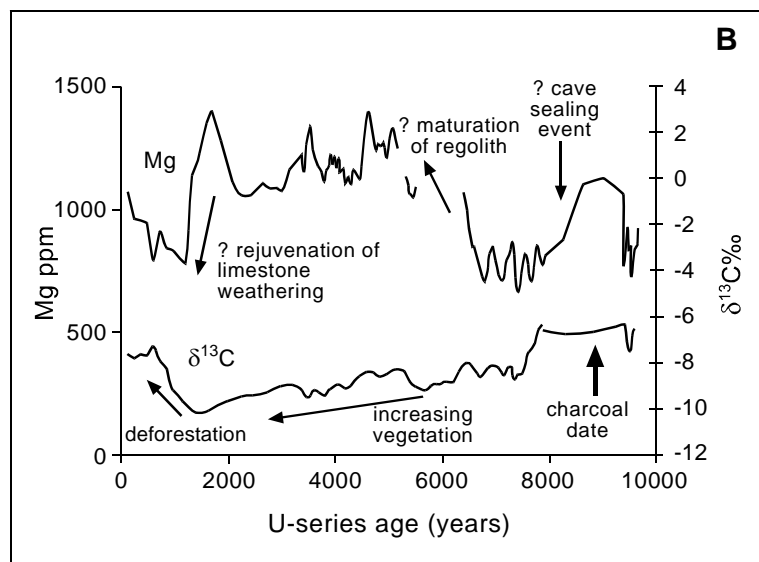
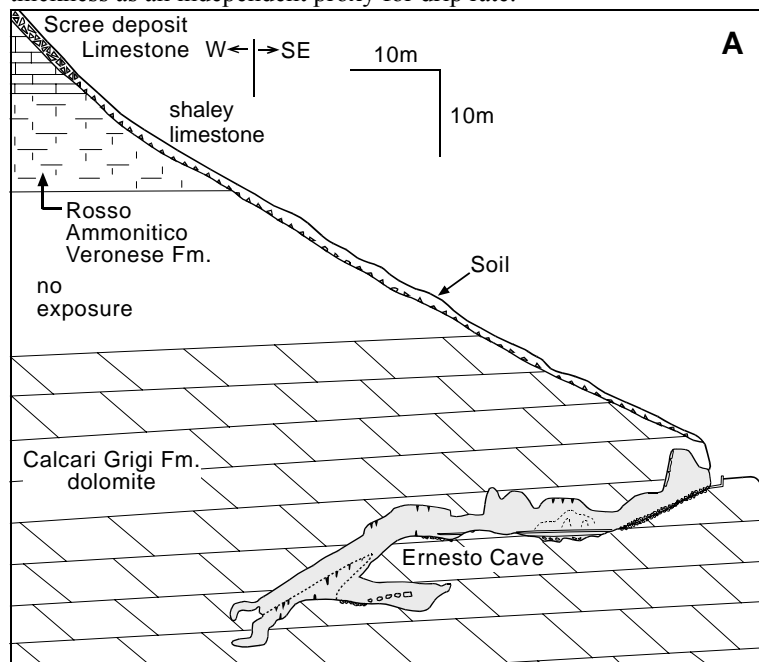
(f) the solution composition varies significantly from pure  $\text{CaCO}_3$  (e.g. pure dolomite aquifer). A contrary case arises when sulphuric acid from pyrite oxidation enhances limestone dissolution (e.g. Atkinson *et al.*, 1983).

Given that the basic geometric aspects of the cave remain relatively constant for long periods, the above data suggest that temperature changes may influence decadal to millennial variations in growth rate of stalagmites. Frisia *et al.* (2003) have shown that the growth rate of speleothems in the Ernesto cave is particularly sensitive to temperature. Proctor *et al.* (2000, 2002) describe a different case from the peat-covered shallow karst system at the Tartair cave in Scotland. Here, a quantitative model was produced by comparison of time series of annual growth rates with instrumental climatic data to support the concept that soil  $\text{CO}_2$  production is more strongly dependent on rainfall than temperature at this site. Relatively dry conditions promote higher  $\text{CO}_2$  production in what would otherwise be a

waterlogged soil, and enhance  $\text{CaCO}_3$  dissolution and speleothem growth.

### 7.5.2 Stalagmite morphology

Curl (1973) extended the insights of Franke (1965) and provided a theoretical analysis of the expected minimum diameter of a stalagmite (around 3 cm), which arises from spreading of a water droplet over a flat surface, in relation to typical volumes of the water drop and thickness of the water film. Dreybrodt (1988, 1999) has further extended the analysis, and the modelled effects of changing water supply are illustrated in Fig. 7.8A,B. Genty and Quinif (1996) have interpreted a Belgian stalagmite in this way using laminae thickness as an independent proxy for drip rate.



Kaufmann (2003) has graphically illustrated the effects of  $\text{PCO}_2$ , temperature and drip rate on speleothem morphology in relation to known long-term climate change. This is an interesting exercise, but too many factors could change over the long intervals being modelled for the results to be considered realistic. A number of stalagmites also have more conical shapes in which significant growth occurs on their flanks.

### 7.6 Summary of use of speleothems in palaeoclimate determination

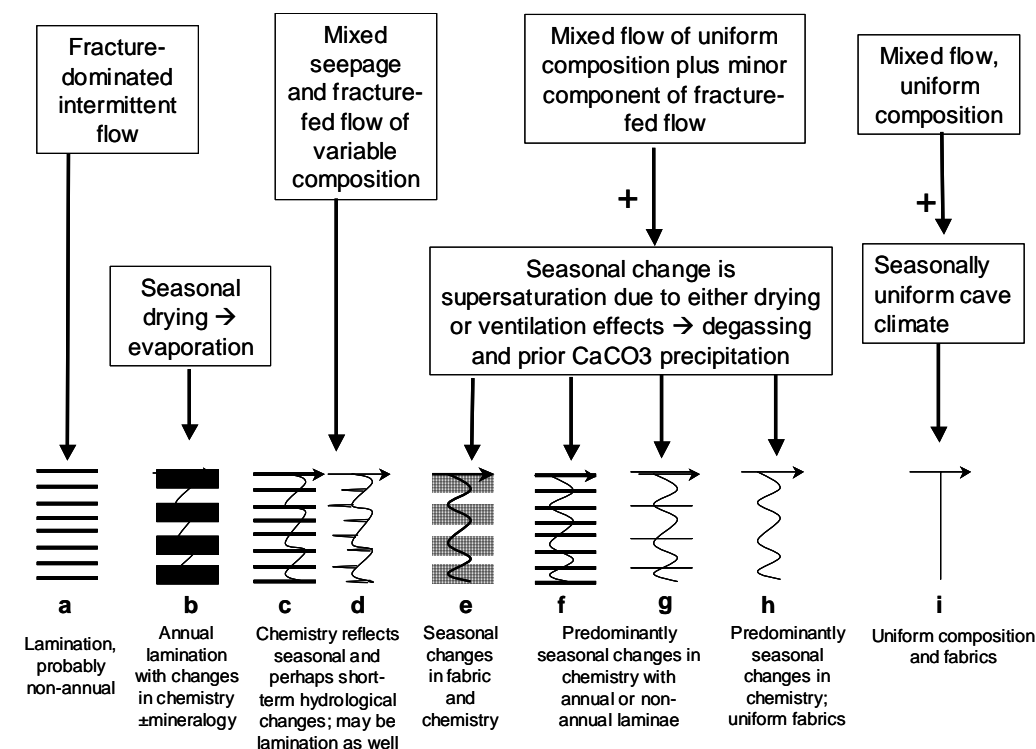
At a coarse level of time resolution, episodes of speleothem growth record relatively wet periods in semi-arid climates, or relatively warm periods in cool temperate climates. The precise dating of speleothems allows them to test Milankovitch theory and to calibrate the timing of palaeoclimate fluctuations. Counting of physical or chemical laminae allows the duration of climatically significant intervals to be determined.

**Figure 7.9:** (A) Cross-section through the Alpine Ernesto cave, Trentino province, Italy. (B) Interpretation of Mg and  $\delta^{13}\text{C}$  records through stalagmite ER76 (McDermott et al., 1999; Frisia et al., 2003) from the cave. The cave is at 1165 m altitude and has a temperature of 6.5 °C. Holocene palaeoclimate reconstructions have been carried out on speleothems using isotopes and fabrics (McDermott et al., 1999), isotopes and trace elements (Frisia et al., 2001) and lamina thickness (Frisia et al., 2003). In these diagrams we highlight other potential controls on long-term evolution. The cave is situated under a steep forested hillside and variations in the degree of forest cover may well have controlled the  $\delta^{13}\text{C}$  composition of the speleothems, with the increase in the last millennium likely related to human-induced deforestation (Frisia et al., 2001). The overlying very thin debris fan feeds from a gully in the cliff of Rosso Ammonitico limestones that overlie the Lower Jurassic dolomites in which the cave is set. Movement of limestone down the fan supplied abundant calcite in the soil overlying the cave in which cave waters derive their characteristic chemistry and which is captured by the speleothems. Arguably, the long-term evolution of the Mg/Ca content of dripwaters and hence the Mg content of speleothems may reflect the geomorphic evolution of the regolith. Intermittent debris movement is required at least until 9 ka, which is the date when an episode of cave occupation, dated by the charcoal in a hearth in the cave. Only micro-mammal remains are found in the cave after this time and it can be inferred that it was closed by debris movement and only re-opened after its contemporary discovery in 1983. The major shifts in Mg content could be interpreted as reflecting changing availability for dissolution of limestone and dolomite fragments in the soil zone, although climatic changes may also be influential.

Used qualitatively, a number of parameters exhibit changes that can be interpreted in palaeoclimatic terms, given an understanding of the directional sense of the calibration. Examples are laminae thickness for temperature or rainfall,  $\delta^{18}\text{O}$  for temperature or rainfall,  $\delta^{13}\text{C}$  for type or amount of vegetation or degree of cave air circulation, Mg and/or Sr for aridity,  $^{87}\text{Sr}/^{86}\text{Sr}$  for rainfall or changes in aeolian activity or source. Quantitative transfer functions have been derived for the above parameters in specific circumstances, but their degree of applicability over time needs to be viewed cautiously. Finally, it should be remembered that the ground surface over caves is often anthropogenically disturbed and speleothems can record this activity. Figure 7.9 illustrates some of the issues that arise when trying to extract palaeoclimate information from

speleothems at sites where both geomorphic and human activity have been prominent in the past.

Several of the parameters mentioned above can yield information at high resolution, even to sub-annual level, and this provides an important frontier area for research. Drawing on the material discussed earlier, Fig. 7.10 provides a first attempt at some qualitative models of the predominant controls on annual scale variations in chemistry and/or fabric



of speleothems, particularly stalagmites.

**Figure 7.10:** Diagrammatic relationships between the flow-related and cave-related geomorphic factors and the high-resolution properties of speleothems (mainly stalagmites). Possible examples are (a) Ballynamintra (Fairchild et al., 2001); (b) Drotsky's Cave, Botswana, Railsback et al. (1994); (c) or (d) Villars (inferred from water chemistry of Baker et al., 2000) (d) Crag cave stalactite (Fairchild et al., 2001), Clamouse (McDermott et al., 1999; Frisia et al., 2002; McMillan et al., 2005); (e) Père-Noël and other Belgian caves, and Villars, France, (Genty and Quinif, 1996; Genty et al., 1997), (f) some Obir stalagmites (Spötl et al., 2005 and unpublished); (g) Ernesto (Huang et al., 2001; Fairchild et al., 2001); Obir (Fig. 7.7c); (h) Crag stalagmite 8.2 ka event (Baldini et al., 2002); (i) not recorded for certain: may only occur in some deep caves.

## 7.7 Directions for future research

Speleothems are so rich in information that there are myriad future directions, some of which are listed as items below:

### (a) speleothem deposition processes

- Experimentation and cave observations on the controls on elemental partitioning between fluid and speleothems;
- Occurrence and extent of kinetic isotope fractionations (experiments and observations);

- Relationships between fluid chemistry and fabrics, including laminae properties;
- Controls on diagenesis in speleothems.

### (b) karst and cave environment

- Climatic controls on cave ventilation;
- Degassing phenomena in relation to speleothem morphology and growth rate;
- Integration of organic geochemical studies and high-resolution monitoring of natural organic tracers;

- Quantitative models of cave-karst aquifer hydrology and hydrogeochemistry allowing the distinction of climatic from cave-specific factors.

### (c) palaeoclimate

- Duplication of time series;
- Multiproxy data sets – data-gathering is some way behind advances in technology at present and new proxies are being discovered every year;
- Integration with other palaeoclimate recorders (e.g. lakes, peat bogs, ice cores, marine records);
- Interchange of information with climatic modellers;
- Testing of forcing models of climate change (orbital, solar, ocean versus atmospheric circulation etc.).

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